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THE EFFECT OF DOPANT TRANSPORT RATE ON CRYSTALLINE DAMAGE IN SI--ETC(U)
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Studies are described of the volatilization of hydrogen B_2O_3 species in control water vapor ambients and the reaction with silicon to form boron silicide which are used to control defects in the silicon.

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THE EFFECT OF DOPANT TRANSPORT RATE ON CRYSTALLINE DAMAGE IN SILICON

Final Report

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January 17, 1980

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DAAG29-76-C-0227

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SUMMARY

The goals of this grant were as follows:

1) To develop a quantitative understanding of the volatilization kinetics of boron glass, B_2O_3, grown on boron nitride diffusion source wafers, in the presence of controlled amounts of water vapor. The water vapor was obtained by adding controlled amounts of hydrogen to an excess oxygen ambient.

2) Determine the growth properties of silicon-boron layers and their role in controlling defects in device structures.

The first aspect of the study involved the calculation of the vapor pressures of HBO_2, H_3BO_3 and $(HBO_2)_3$ for the reaction of B_2O_3(liquid) with $H_2O(g)$.

The results of the volatilization experiments are:

1) The volatilization of B_2O_3 (ℓ) in dry nitrogen from an activated BN wafer occurs much more rapidly than the theoretical predictions of the Hertz-Langmuir equation for $B_2O_3(\ell) \rightarrow B_2O_3(g)$. The prediction of the volatilization rate of HBO_2 according to the Hertz-Langmuir equation with a small amount of H_2O present shows good agreement with the observed experimental results.

2) The oxidation in the initial "activation" at 900°C was, in the early stages, parabolic and gradually approached a linear relationship after ≃ 2 hours. This result follows from an oxidation reaction with concurrent vaporization of the oxide when the initial rate of weight gain (due to parabolic oxidation) is more rapid than the linear volatilization rate.

3) The rates of volatilization with the addition of varying amounts of water vapor agree with the predictions that HBO_2 is the important volatile species at 1000°C and lower H_2O contents and H_3BO_3 and/or $(HBO_2)_3$ are the important volatile species at 800°C at higher H_2O contents.

4) The rates of oxidation are a complex function of temperature and carrier gas composition. The observed rate of oxygen consumption appears to be exponentially dependent on temperature with a ΔH of ≃40Kcal/mole.

5) The rate of volatilization varies approximately by a factor of 3 for 3 vol.% H_2O between 800 and 1000°C as the predominant vapor species change from (H_3BO_3) and $(HBO_2)_3$ at 800°C to about 75% HBO_2 and 25% of the other two species at 1000°C. At lower water vapor contents the rate of volatilization increases more rapidly than at 3 vol.% H_2O as predicted from the total pressure of the volatile species at these lower partial pressures of H_2O.

The results of the characterization of the boron silicide layers formed during the boron glass reaction with the silicon after the hydrogen is added to the ambient to form HBO_2 are:

1) The boron rich layer is a multiphase reaction product containing (depending on the details of the processing conditions) SiB_4, SiB_6 and amorphous boron with some degree of dissolved oxygen. The relative concentrations of the various constituents vary with variable process time and temperature.

2) The formation of the boron rich layer when using the hydrogen injection process, is diffusion rate dependent. This diffusion dependence is probably due to the diffusion of boron through the reaction layer to the silicon surface.

3) The diffusivity of boron through the reaction layer has been determined from the reaction rate constant and follows the equation in the temperature range of 850°C to 1050°C as shown:

$$D_{B_{SiB}} = 1.8 \times 10^{-3}\, e^{-2.76/kT}\ (cm^2/sec)$$

4) The presence of the boron rich layer results in a decreased concentration of extrinsic stacking faults. This effect is heightened with increasing process time and temperature.

5) Extrinsic stacking fault annihilation can be caused by either of two mechanisms.

i) The stacking faults near the surface are simply consumed by the encroaching reaction layer as it forms; or, more likely.

ii) Annihilation occurs by a silicon vacancy condensation in the extrinsic stacking faults at the reaction interface.

PAPERS AND PUBLICATIONS

1) "Volatization from Oxidized Boron Nitride Solid Diffusion Sources During Hydrogen Injection," D. L. Johnson, R. E. Tressler, J. Stach, paper presented at Electrochemical Society Meeting, May 1978, Seattle, WA, submitted for publication to Electrochemical Society Journal, revisions currently being made.

2) "Investigation of Growth Characteristics of the Boron Rich Layer Formed During Hydrogen Injection," T. Facey, R. E. Tressler, I. S. T. Tsong, J. Stach, recent newspaper at Electrochemical Society Meeting, October 1978, Pittsburgh, PA.

3) "The Use of Boron Rich Layer Formation During Boron Deposition as a Method of Crystal Defect Elimination in Silicon," T. Facey, R. E. Tressler, J. Stach, to be presented at Electronic Components Conference, April 1980, San Francisco, CA.

4) "Characterization of Boron Silicide Formed During Hydrogen Injection Processes," T. Facey, I. S. T. Tsong, R. E. Tressler, J. Stach, manuscript in preparation for submission to Electrochemical Society Journal.

5) "Defect Control Mechanisms Using Boron Silicide Layers," T. Facey, R. E. Tressler, J. Stach, manuscript in preparation for submission to Electrochemical Society Journal.

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